COATINGS AND ENAMELS

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ANTIBACTERIAL COMPOSITE GLASS COATINGS FOR PROTECTING SPECIAL-PURPOSE STEEL PANELS

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It is confirmed that glass enamel coatings are promising for antibacterial protection of steel panels. A methodological approach is developed for obtaining antibacterial composite glass coatings. A glass matrix with a programmed structure, bactericide nanopowders of zinc phosphate, and composite glass coatings based on them have been obtained on the basis of the system $R_2O – RO – TiO_2 – P_2O_5 – SiO_2$. The composition of a coating with the maximum antibacterial effect with respect to E. Coli bacteria is determined.

Key words: antibacterial protection, glass enamel coatings, syntheses of glass matrix.

One of the most important social and materials-engineering problems today is providing reliable long-term antibacterial protection of objects used by humans. This is due to a desire to increase the quality of life, to an increase in epidemics with different etiology, specifically, SARS and types of chicken and swine flu, which claim thousands of human lives every year, as well as to the low effectiveness of existing solutions in fighting the multiplication of pathogenic bacteria.

In this connection, a great deal of attention is being focused on developing and using antibacterial materials in different areas of industry and in the home: plastics and special glasses as well as composite, metallic, polymer, glass ceramic, and glass enamel coatings. The effectiveness and promise of glass enamel coatings in particular are due to their large advantages over other materials [1].

Because of their combination of properties, such as chemical stability, mechanical strength, heat resistance, resistance to bio-corrosion, as well as aesthetic-decorative properties, i.e., because functional and hygienic properties are present simultaneously, glass enamel coatings are used worldwide to protect widely used metal articles. Together with hygienic action, antibacterial action is also an important usage characteristic of glass enamel coatings [2].

The rapid development of architectural – construction industry throughout the world has made it necessary to develop and adopt competitive universal protective-decorative coatings for steel panels to be used in medical, pharmaceutical, sanitary-technological applications, among which glass enamels with antibacterial functions with respect to a wide spectrum of harmful micro-organisms have a special place.

Even though there is an urgency to obtaining and using such coatings and our domestic enameling industry is well developed, large-scale research in this direction is not be conducted in the Commonwealth of Independent States. For this reason, our objective in the present work, which is devoted to the problem described — the development of antibacterial glass enamel coatings for protecting steel panels of operating units in medical institutions — was to develop a methodological approach to synthesizing such coatings and to determine their optimal composition for E. Coli bacteria.

The physical-chemical and usage properties of the enamels developed for indoor architectural panels must meet the following requirements [3]:

guaranteed antibacterial effect against gram-negative and gram-positive microbes (99% destruction of harmful bacteria after 24 h);

chemical resistance and water resistance no lower than ISO 2742 class;

enamel coating no more than 0.4 mm thick;

adhesion no less than 3 units on the ISO 2723 scale;

prescribed aesthetic-decorative characteristics (color, sheen, and so on).

It is well known [4] that the idea of combining the multifunctionality of glass enamel coatings with bactericidal ac-

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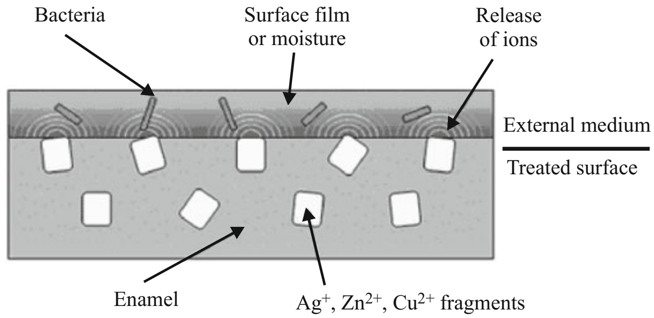

Fig. 1. Mechanism of the effect of ions of bactericidal metals on pathogenic bacteria.

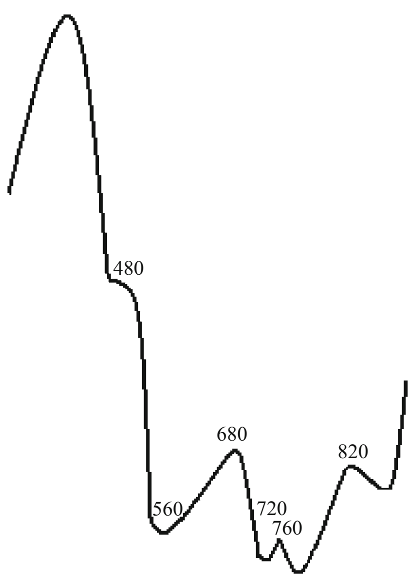

Fig. 2. Thermogram of the glass KF 11 (the temperature in °C is indicated on the curve).

tion of the cations Ag^+, Zn^{2+}, Cu^{2+}, and others is the basis for obtaining antibacterial coatings.

The bactericidal properties of the ions of these metals, specifically, silver, are oligodynamic. The destruction of microorganisms is a result of the formation of free ions, which are absorbed on the cell surfaces and react with groups of SH enzymes and proteins (Fig. 1).

There are two known methods for introducing bactericidal cations into glass: in the form of initial oxide components added to the enamel mix and in the form of special nanopowders — ground ready-made frit. To obtain antibacterial glass enamel coatings, in the present work we introduced bactericidal nanopowders into the glass enamel matrix. The structure of this glass matrix must ensure a prescribed orientation of the cations of the bactericidal metals and uniform arrangement of the cations in the surface layer of the coating. The main factor determining the prescribed orientation of the cations is the presence calcium phosphates in the glasses and coatings based on them, since it is the structure of these phosphates that can served a carrier of the cations of the bactericidal metals, specifically, Zn^{2+} and Cu^{2+} [5].

Zinc was chosen at the bactericidal cation because of zinc ions can replace Ca^{2+} isomorphically in the structure of the glass matrix and give an antibacterial effect without being harmful to humans. The character of the distribution of the cations, which must be uniform, and the presence of a glass composite containing the glass matrix with finely dispersed calcium phosphate crystals are very important. For this, it is necessary to ensure directed crystallization of a glass matrix with a prescribed composition; the result is the formation of calcium phosphates.

The following system was chosen as the initial system to synthesize the glass matrix: $R_2O – RO – TiO_2 – P_2O_5 – SiO_2$, where R_2O — Na_2O, Li_2O and RO — CaO. A region of glass formation was chosen in it and 12 compositions of the model glasses, differing by the content of CaO and P_2O_5 and their ratio, were synthesized. The presence of a crystalline phase in these glasses and its composition after founding were determine by means of differential – thermal and x-ray phase analyses. The character of the post-heat-treatment distribution of the crystalline phase in the glass composite was investigated by means of optical microscopy of samples obtained by the gradient-thermal method.

It was determined that KF 9, KF 10, and KF 11 glass with molar content 4 – 5% P_2O_5 and 6 – 10% CaO with CaO/P_2O_5 ratio 1.5, 1.75, and 1.6, respectively, formed a finely dispersed structure with hydroxyapatite crystals. This is confirmed by the thermograms obtained for these materials. Specifically, a negligible outlined area of the endothermal effect prior to the exothermal effect, corresponding to crystallization, is observed for the KF 11 composition. This shows that only a small number of nucleation centers are formed and that this glass does not crystallize intensively with formation fine hydroxyapatite crystals (Figs. 2 and 3).

Zinc phosphates with particle size of the order of 10 nm were obtained by chemical precipitation to be used as bactericidal fillers. This filler was added during wet grinding to the KF 9 – KF 11 glass composite obtained beforehand. The slips were deposited on 0.7 mm thick samples of low-carbons steel after which the coatings were dried and annealed at 800 – 820°C.

The antibacterial activity of the enameled surface was determined as the degree to which the

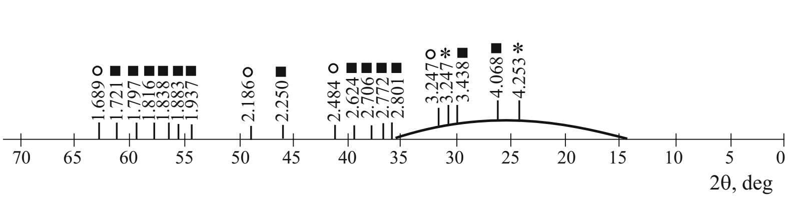

Fig. 3. Diffraction pattern of the glass composite KF 11: ✱) SiO_2 quartz; ○) TiO_2 rutile; ■) $Ca_5(PO_4)_3OH$.

TABLE 1. Antibacterial Effect of the Glass Coatings Studied

Glass enamel coating	Number of E. Coli bacteria in the nutrient medium		Antibacterial effect, %
	before contact enamel	after contact with enamel	
ÉSP-117	$\approx 2 \times 10^3$	1.1×10^3	45
ÉSP-117 + $Zn_3(PO_4)_2$	$\approx 2 \times 10^3$	4×10^2	80
ÉSP-5	$\approx 2 \times 10^3$	1.2×10^3	40
ÉSP-5 + $Zn_3(PO_4)_2$	$\approx 2 \times 10^3$	6×10^2	70
KF 9	$\approx 2 \times 10^3$	8×10^2	60
KF 10	$\approx 2 \times 10^3$	9×10^2	55
KF 11	$\approx 2 \times 10^3$	7×10^2	65
KF 9 + $Zn_3(PO_4)_2$	$\approx 2 \times 10^3$	2×10^2	90
KF 10 + $Zn_3(PO_4)_2$	$\approx 2 \times 10^3$	2×10^2	90
KF 11 + $Zn_3(PO_4)_2$	$\approx 2 \times 10^3$	0	100

growth of bacteria in it decreased (see Table 1). Coatings obtained from the covering titanium enamels ÉSP-117 and ÉSP-5 without bactericidal powders and with additions of zinc phosphate are tested for comparison.

It was determined that all glass enamel and glass composite coatings studied are characterized by a definite antibacterial effect. Thus, it equaled 45 and 40% for ÉSP-117 and ÉSP-5 glass enamels, respectively, and 55 – 65% for KF 9 – KF 11 without zinc phosphate additives. The introduction of 1 – 5 wt.% $Zn_3(PO_4)_2$ substantial increased antibacterial activity in all cases. The highest level of this indicator was observed with a KF 11 coating containing zinc phosphate [6].

In summary, it has been confirmed that glass enamel coating are promising for antibacterial protection of steel panels. A methodological approach for obtaining antibacterial glass composite coatings has been developed. A glass matrix with a prescribed structure, bactericidal nanopowders of zinc phosphate, and glass composite coatings based on them were obtained on the basis of the system $R_2O - RO - TiO_2 - P_2O_5 - SiO_2$. The composition of the coating with maximum antibacterial effect with respect to E. Coli bacteria was determined.

REFERENCES

1. F. Marzullo, *Indagine Bacteriologica Comparata*, Centro Smalti Porcellanti (2001).
2. L. L. Bragina and A. P. Zubekhin (eds.), *Technology of Enamel and Protective Coatings* [in Russian], NTU "KhPI," Kharkov, YuRGTU (NPI), Novocherkassk (2003).
3. *Quality Requirement*, European Enamel Authority (2004), 2nd Edition.
4. E. Voß and C. Störch, "Evaluation of bacterial growth on various materials," in: *Proc.20th Intern. Enameller Congress*, Istanbul, Turkey, May 15 – 19, 2005, pp. 194 – 210.
5. A. Dopan, A. Genser, and C. Pekcen, "Calcium phosphate based antibacterial ceramic powder containing enamel," *ibid.*, pp. 239 – 244.
6. L. L. Bragina, O. V. Savvova, O. V. Shalygina, Ya. A. Pokroeva, and G. K. Voronov, "Ukrainian Patent No. 86720, MKI[6] C03C8/08, C23 D 5/00, Complex silicophosphate glass enamel coating, No. a 2008 06235," Application May 12, 2008; published May 12, 2009; *Byul. Izobr.*, No. 9 (2009).